

## An Empirical Formula Expressing the Mutual Dependence of C—C Bond Distances\*

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An empirical formula is suggested to describe the mutual dependence of the length of the bonds formed by a central atom in systems built up from equivalent carbon atoms, e. g. diamond, graphite, the cumulene and polyene chains and intermediate structures between them. A geometrical representation of the relationship is a regular tetrahedron. A point of this tetrahedron characterizes the arrangement of the atoms around the central one. From the position of the point the bond distances — and possibly the bond angles — can be deduced.

Experimental bond length determinations have made clear in the last few decades that the C—C bond distances vary over a relatively long range, from about 1.2 Å to about 1.6 Å. There were several attempts to correlate these bond distances on empirical way to different factors like double-bond character,<sup>1,2</sup>  $\pi$ -bond order,<sup>3</sup> state of hybridization,<sup>4,5</sup> the number of adjacent bonds,<sup>6</sup> or the overlap integrals.<sup>7</sup> Recently a new empirical formula has been suggested to describe the mutual dependence of the C—C bond distances.<sup>8</sup> The subject of this paper is the interpretation of this empirical equation.

Carbon has three allotropic modifications: diamond, graphite and the not completely characterized chain form<sup>9,10</sup> (carbynes). The chain can have cumulene or polyene structure. The constituent atoms of a given modification can be considered to be equivalent, i. e. they form the same number and the same type of covalent bonds. The arrangement of the covalently linked atoms around the central one is tetrahedral, trigonal or linear (Figure 1). The following empirical formula is suggested to describe the mutual dependence of the length of the bonds ( $r_i$ ) formed by a central carbon atom with  $n$  other equivalent atoms.

$$\sum_{i=1}^n \frac{1}{r_i - 0.9233} = 4.7935 + 0.4114 n \quad (1)$$

$$n = 2, 3, 4$$

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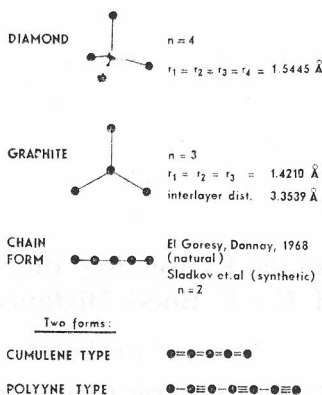


Figure 1. Arrangement of atoms in the three allotropic modifications of carbon.  $n$ : number of covalent bonds formed by the central atom,  $r$ : bond length.

When the length of all bonds are the same  $r$  can be expressed in function of  $n$ .

$$r = \frac{n}{4.7935 + 0.4114 n} + 0.9233 \quad (2)$$

The  $r$  values calculated by the equation — including their lower and upper limit at  $n = 1$  and  $n = \infty$ , respectively — are summarized in Table I. It is a question whether the shortest length has any physical significance. Formally it can be considered as the bond length of a hypothetical  $C_2$  ( $C \equiv C$ ) molecule which, however, is by no means identical with the experimentally detected unstable  $C_2$  fragment. The experimental bond distances of diamond and graphite are accurately reproduced.

When the central atom forms two kinds of bonds ( $m$  bonds of  $r_m$  kind and  $n-m$  bonds of  $r_{n-m}$  kind) the length of one type of bonds ( $r_{n-m}$ ) can be calculated from that of the other ones ( $r_m$ ).

$$r_{n-m} = \frac{n-m}{4.7935 + 0.4114 n - \frac{m}{r-0.9233}} + 0.9233 \quad (3)$$

$$n = 2, 3, 4$$

$$n > m = 1, 2, 3$$

TABLE I  
Dependence of Bond Length on the Number of Bonds

$n$	$r$ (Å)	
	Calc. by eq. 2	Experimental <sup>11</sup>
1	1.1154	
2	1.2794	1.292 <sup>a</sup>
3	1.4210	1.4210
4	1.5445	1.5445
$\infty$	3.3540	3.3539 <sup>b</sup>

a: Calculated by the MINDO method<sup>12</sup>. b: The interlayer distance of graphite.

This formula (at  $n = 2$  and  $m = 1$ ) is suitable for checking the empirical equation by experimentally determined polyynes and cumulene type bond distances. Replacement of  $r_m$  by 1.384, the single C—C bond length of diacetylene,<sup>13</sup> gives 1.214 Å for  $r_{n-m}$ . This is exactly the length of the triple bond in dimethyl-acetylene.<sup>14</sup> If 1.300 is taken for  $r_m$ , then the calculated  $r_{n-m}$  is 1.261 Å. This is in good agreement with the bond distances in the central part of a cumulene (1.300 and 1.260 Å).<sup>15</sup>

It is well known that the structure of graphite can be derived from that of diamond by lengthening one bond of every carbon atom to the interlayer distance of graphite (Figure 2). This structural relation is also reflected by

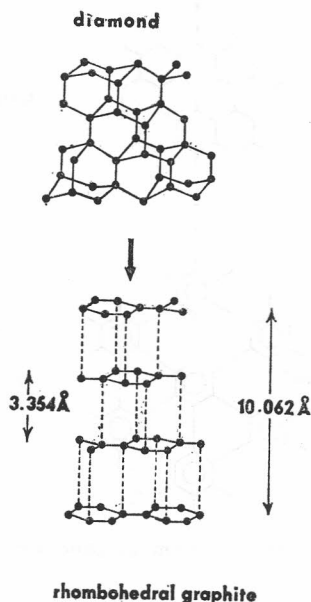


Figure 2. Structural relation of diamond and rhombohedral graphite.

eq. 3. Replacement at  $n = 4$  and  $m = 1$  of  $r_m$  by the interlayer distance (3.3539 Å) gives 1.421 Å — that is the experimental inlayer distance of graphite — for the length of the remaining three bonds ( $r_{n-m}$ ).

The equations are supposed to describe the bond distances in intermediate structures, too, if they are built from equivalent atoms. These hypothetical intermediate structures can be derived from the allotropic modifications by lengthening or shortening one or more bonds of every atom to given lengths and leaving the rest of the bonds to shorten or lengthen, respectively, to distances determined by their mutual dependence. For example, by lengthening one or two bonds in graphite to 1.477 Å a »polybenzene« or a »polyolefin« structure, respectively, can be derived (Figure 3). The calculated length of the shortened bonds are 1.397 and 1.337 Å, the same as the experimental C—C bond distances of benzene and ethylene, respectively.

Eq. 1 at  $n = 3$  defines a concave surface shown in Figure 4. Its center corresponds to graphite. The hypothetical »polybenzene« and »polyolefin« structures are found on the line indicated by the intersecting plain. The three

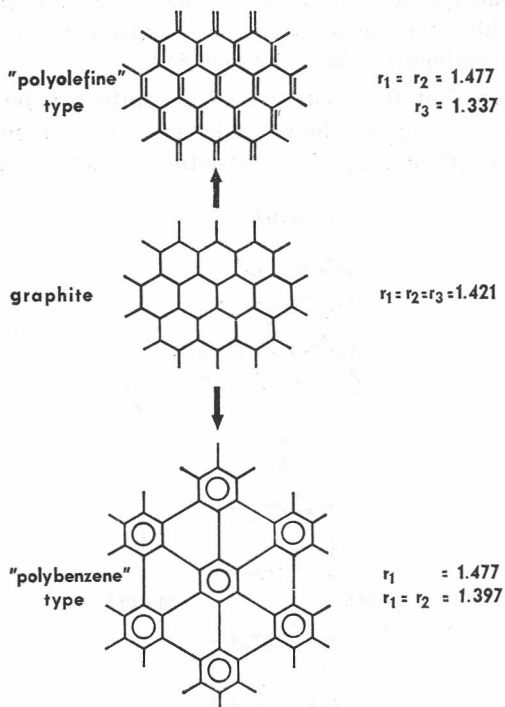


Figure 3. Hypothetical structures derived from graphite by lengthening one or two bonds.

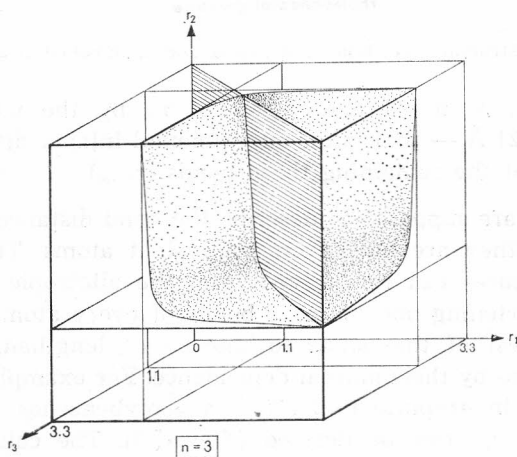


Figure 4. Graphic representation of equation 1 at  $n = 3$ . The center of the concave surface corresponds to graphite.

edges (the hyperbolas on the faces of the cube) and the three vertices represent the chain forms ( $n = 2$ ) and the hypothetical  $C_2$  molecule ( $n = 1$ ), respectively. At  $n = 4$  Eq. 1 defines a four dimensional body — with diamond in its center.

In order to facilitate the graphic representation at  $n = 4$  in three dimensions, a new parameter ( $I$ ) is derived from the bond length.

$$I = \frac{0.8345}{r - 0.9233} - 0.3434 \quad (4)$$

$I$  values calculated from different characteristic C—C distances are summarized in Table II. It can be seen that  $I$  varies from 0 to 4. By use of  $I$  eq. 1 simplifies to

$$\sum_{i=1}^n I_i = 4 \quad (5)$$

or

$$\sum_{i=1}^4 I_i = 4 \quad (6)$$

TABLE II

Calculated  $I$  Values of Characteristic C—C Bonds

	$r$ (Å)	$I$
graphite (interlayer)	3.3539	0
diamond	1.5445	1.000
ethane	1.533	1.025
butadiene ( $C_2 - C_3$ )	1.465	1.197
graphite	1.421	1.333
benzene	1.397	1.418
diacetylene ( $C_2 - C_3$ )	1.384	1.468
ethylene	1.337	1.674
allene	1.3116	1.806
cumulene	1.300	1.872
cumulene	1.279	2.000
cumulene	1.260	2.135
acetylene	1.212	2.547
$C_2$ (hypothetical)	1.1154	4.000

In the later case the number of really existing bonds ( $n$ ) is completed to 4 with  $4 - n$  hypothetical ones having zero  $I$  values. This makes possible to characterize the systems built up from equivalent carbon atoms by four  $I$  values (Table III). Since they are not independent it is sufficient to know three of them.

TABLE III

Characterization by  $I$  Values of Systems Built up of Equivalent Carbon Atoms

	$n$	$I_1$	$I_2$	$I_3$	$I_4$
diamond	4	1	1	1	1
graphite	3	1.333	1.333	1.333	0
cumulene	2	2	2	0	0
polyyne	2	1.468	2.532	0	0
$C_2$ (hyp.)	1	4	0	0	0

Eq. 6 can be represented by a regular tetrahedron (length of edges: 4 units). The point in the center corresponds to diamond. Its position — like that of any other point — can be defined by three  $I$  values, that is, by the intersection of three planes as shown in Figure 5. Graphite, the »polybenzene«

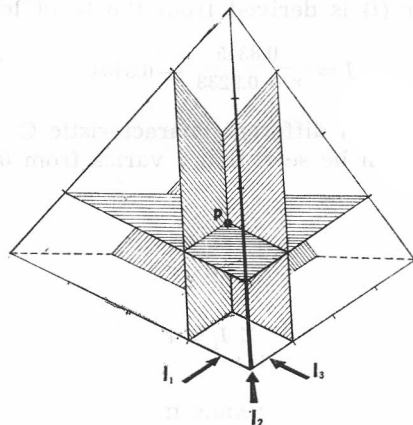


Figure 5. Graphic representation of equation 6. The center of the regular tetrahedron corresponds to diamond. It is defined by three planes parallel with three different faces.  
 $I_1 = I_2 = I_3 = 1$ .

and the »polyolefin« structures are represented on the faces, while the chain forms and the hypothetical  $C_2$  are found on the edges and vertexes, respectively (Figure 6).

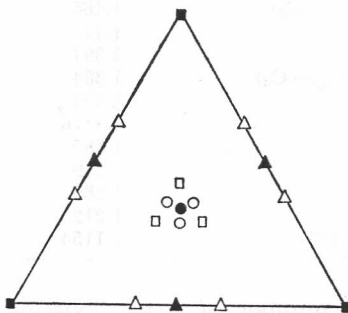


Figure 6. One of the faces of the tetrahedron. ●: graphite, ○: »polybenzene«, □: »polyolefin«, ▲: cumulene, △: polyyne, ■: hypothetical  $C_2$ .

Position of the point characterizing the geometrical state of the system defines the  $I$  values and indirectly (through eq. 7) the bond distances.

$$r = 0.9233 + \frac{0.8345}{I + 0.3434} \quad (7)$$

Bond angles seem to be deducible from the position of the point, too, by drawing lines through the vertexes as shown in Figure 7. As far as diamond, graphite and the linear chain forms are concerned the deduced angles coincide exactly with the experimental ones:  $109,5^\circ$ ,  $120^\circ$  and  $180^\circ$ , respectively. It is a question, however, how reliable the deduced bond angles are in the case of intermediate structures. As shown in Figure 8 (see also Figure 6) the olefinic bond angles are at least qualitatively correct.

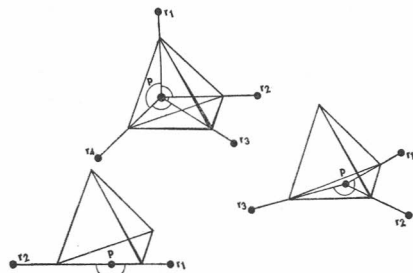


Figure 7. Deduction of the bond angles from the position of the characteristic point (P).

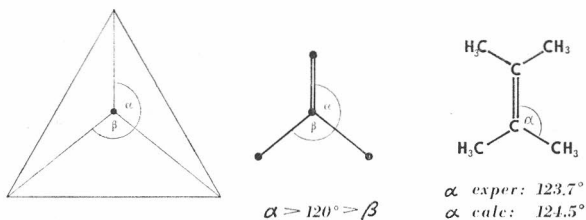


Figure 8. Bond angles in the »polyolefin« structure.

#### REFERENCES

1. L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Amer. Chem. Soc.* **57** (1935) 2705.
2. L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59** (1937) 1223.
3. C. A. Coulson, *Proc. Roy. Soc. London* **A169** (1939) 413.
4. M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5** (1959) 166.
5. B. M. Mikhailov, *Tetrahedron* **21** (1965) 1277.
6. B. P. Stoicheff, *Tetrahedron* **17** (1962) 135.
7. Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.* **92** (1970) 424.
8. A. Furka, *Proceedings of the 2nd European Symposium on Organic Chemistry*, Abstracts of Papers p. 267, Stresa, Italy, 1981.
9. A. El. Goresy and G. Donnay, *Science* **161** (1968) 363.
10. A. M. Sladkov, V. I. Kasatochkin, Yu. P. Kudryavtsev, and V. V. Korshak, *Izv. Akad. Nauk. USSR, Ser. Khim.* (1968) 2697.
11. *Tables of Interatomic Distances and Configurations in Molecules and Ions*. The Chemical Society, Special Publication No. 11. Burlington House, W1. London, 1958.
12. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.* **97** (1975) 1294.
13. M. Tanimoto, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.* **44** (1971) 386.
14. M. Tanimoto, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.* **42** (1969) 2519.
15. H. Irgartinger and H.-V. Jäger, *Angew. Chem.* **88** (1976) 615.

#### SAŽETAK

**Empirijska formula koja prikazuje međusobnu ovisnost duljine C—C veza**

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Predložena je empirijska formula koja opisuje međusobni odnos duljine veza centralnog atoma u sistemima sastavljenim od ekvivalentnih ugljikovih atoma, kao što su npr. dijamant, grafit, kumulenski i poliinski lanci, i u intermedijarnim strukturama. Geometrijska reprezentacija odnosa jest pravilni tetraedar. Točkom toga tetraedra karakteriziran je raspored atoma oko jednoga centralnog atoma. Iz pozicije točke mogu se izvesti duljine veza i eventualno kutovi između veza.

## Comparison of the Heats of Formation<sup>‡</sup> of Hydrocarbons\*

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In order to facilitate the demonstration of the structure dependent stabilizing or destabilizing energy effects characterizing the individual hydrocarbons it is suggested to replace graphite and hydrogen as reference substances (used in calculating the heats of formation) by the series of n-alkanes. This can be achieved by converting the heats of formation into relative enthalpies ( $H_{rel}$ ). The proposed simple equation yields zero for the  $H_{rel}$  of n-alkanes and thus the extra stabilizing or destabilizing effects caused for example by branching or unsaturation, respectively, in other types of compounds are directly expressed by the numerical value of their  $H_{rel}$ .

When teaching organic chemistry it is often needed to demonstrate the structure dependent stabilizing or destabilizing effects. For this purpose either the heats of formation ( $\Delta H_f$ ) or the heats of properly chosen reactions — for example heats of hydrogenation — are compared. It has to be taken into account, however, that a considerable fraction of the  $\Delta H_f$  of a compound is arising from the mere combination of its constituent elements (since the elements are the reference substances) and this part often masks the contribution of the structural differences.  $\Delta H_f$  is strongly dependent on composition and, as a consequence, comparisons are meaningful only when isomers are concerned. Heats of hydrogenation can be used to compare to one another the stability of different alkenes regardless of their composition. They do not really express, however, the stability difference between an alkene and its saturated derivative\*\*.

The purpose of this paper is to show that in the case of hydrocarbons the disturbing effect due to the differences in composition can be eliminated by replacing carbon and hydrogen as reference substances by n-alkanes. This can be realized by converting  $\Delta H_f$  of the hydrocarbons into relative enthal-

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‡ Heats of formation and heats of reaction mean enthalpies of formation and enthalpies of reaction, respectively. The data taken from three sources<sup>1,2,3</sup> refer to gas phase and are expressed in kJ/mole.

\*\* The heat of hydrogenation in fact represents the difference between the  $\Delta H_f$  values of the two compounds which, however, are not isomers.



pies\* ( $H_{\text{rel}}$ ) defined by the following equation\*\*, where  $n_{\text{C}}$  and  $n_{\text{H}}$  are the number of carbon and hydrogen atoms, respectively.

$$H_{\text{rel}} = \Delta H_{\text{f}} - 22.822 n_{\text{C}} + 21.72 n_{\text{H}}$$

$H_{\text{rel}}$  values calculated from  $\Delta H_{\text{f}}$  of several representatives of different classes of hydrocarbons are summarized in Tables I and II. These data show

TABLE I  
*Relative Enthalpies of Some Acyclic Hydrocarbons<sup>a</sup>*

	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>
n-alkanes	0	1	0	0	0	0
2-Me-alkanes		-9	-8	-7	-7	-7
2,2-diMe-alkanes		-19	-18	-18	-16	-18
1-alkenes	93	82	82	82	82	82
konj. polyenes			149		207	
1-alkynes	225	204	204	204	204	204

<sup>a</sup> Data in kJ/mole, C<sub>2</sub>—C<sub>7</sub>: number of carbon atoms in the unsubstituted chain, Me: methyl,  $H_{\text{rel}}$  of methane not included above: -11.

TABLE II  
*Relative Enthalpies of Some Cyclic Hydrocarbons*

	$H_{\text{rel}}$ kJ/mole		$H_{\text{rel}}$ kJ/mole
cyclopropane	115	benzene	76
cyclobutane	109	naphthalene	97
cyclopentane	26	azulene	225
cyclohexane	1	anthracene	129
cycloheptane	25	phenanthrene	105
cyclohexene	75	triphenylene	109
1,3-cyclohexadiene	145	tetracene	142
cyclooctatetraene	289	perylene	113

that the structural effects like stabilization due to branching or destabilization caused by unsaturation or ring strain are directly expressed by the numerical value (including sign) of  $H_{\text{rel}}$ . It is important to note that  $H_{\text{rel}}$  does not depend on chain length or on composition and consequently  $H_{\text{rel}}$  values of non-isomers can be compared to one another without difficulty. The possibility of such comparisons is particularly important when more than one structural effect is operating in the molecule.

Preliminary studies show that the use of relative enthalpies in teaching can be extended to all classes of organic compounds, and in addition, they are expected to facilitate the comparison with the experimental data of some theoretically deduced quantities such as the different types of resonance energies.<sup>4,5,6</sup>

\* The heats of formation themselves can be considered as relative enthalpies, too.

\*\* The constants were determined by the least-squares method from  $\Delta H_{\text{f}}$  of n-alkanes.

## REFERENCES

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, Inc., New York, 1969.
2. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, New York, 1970.
3. R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, W. R. Roth, and G. Schröder, *J. Amer. Chem. Soc.* **95** (1973) 8605.
4. M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.* **87** (1965) 685, 692.
5. L. J. Schaad and B. Andes Hess, Jr., *J. Amer. Chem. Soc.* **94** (1972) 3068.
6. I. Gutman and N. Trinajstić, *Acta Chim. Acad. Sci. Hung.* **91** (1976) 203.

## SAŽETAK

## Usporedba toplina stvaranja ugljikovodika

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Radi lakše demonstracije stabilizirajućih ili destabilizirajućih energijskih efekata ovisnih o strukturi, koji karakteriziraju pojedine ugljikovodike, predložena je zamjena grafita i vodika kao referentnih supstancija (za izračunavanje toplina stvaranja) nizom n-alkana. To se može postići preračunavanjem toplina stvaranja u relativne entalpije ( $H_{rel}$ ). Predložena jednostavna jednadžba daje nulu za  $H_{rel}$  n-alkana, i njome su posebni stabilizirajući ili destabilizirajući efekti, uzrokovani na primjer grananjem ili nezasićenjem u drugim tipovima spojeva, izraženi numeričkom vrijednošću njihove  $H_{rel}$ .